Pretreatment of antibiotics-contaminated waste biological sludge by ozonation

Bosevski I.[1], Kalčikova G.[1], Derco J.[2], Žgajnar Gotvajn A.[1,*]

[1] University of Ljubljana, Faculty of Chemistry ad Chemical Techology, Ljubljana, Slovenia
[2] Slovak Technical University, Faculty of Chemistry and Food Technology, Department of Environmental Engineering, Bratislava, Slovakia [4]

*corresponding author: e-mail: andreja.zgajnar@fkkt.uni-lj.si

Abstract
Ozonation was studied as a pretreatment method for a waste biological sludge, contaminated with large amounts of globally used antibiotics; tiamulin, levofloxacin and amoxicillin. At the concentrations of over 100 mg L^{-1}, these antibiotics were found to inhibit biogas production (up to 50%), which means, that the molecules would pass the anaerobic digestion system unchanged. Ozonation of sludge, contaminated with antibiotics, not only removes inhibitory effects, but also improves overall biogas production for 10% or even more, depending on the dose of the oxidant applied in the pretreatment.
Keywords: Biological sludge, antibiotics, pretreatment, ozone, biogas production

1. Introduction

Widespread use of antibiotics is a notable source of environmental pollution, especially concerning environmentally persistent molecules lately referred as emerging pollutants. Important source of such type of compounds are also wastewater treatment plants, where persistent antibiotics originated from industrial and municipal wastewaters are concentrated and adsorbed on waste biological sludge. Main method for stabilization and utilization of such sludge is anaerobic digestion where inhibition due to the presence of antibiotics could severe interfere with efficiency of biogas production. In that context, ozonation not only enhances biogas production by hydrolysis and nutritional use of organic materials (Venturin et al., 2019), but also removes inhibitory effects of antibiotics present in the substrate by altering the structure of organic substrates in the waste, which is become more accessible to microorganisms and as a consequence improve biogas production (Wacławek et al., 2018). In scope of our study, we have scanned antibiotics from three different molecule groups, aiming to prove literature predictions to actual molecules.

2. Methods

Effects of ozonation to biogas production in anaerobic digestion of waste biological sludge, contaminated with large amounts of antibiotics: tiamulin (animal health), levofloxacin (fluoroquinolone, human use) and amoxicillin (beta lactam, human use) were studied. Biological sludge was taken from a municipal wastewater treatment plant (WWTP) and spiked with antibiotic. In parallel we had four samples to compare; non-treated sludge, ozonated sludge, sludge contaminated with antibiotics, and contaminated and subsequently ozonated sludge. All tests were run in up to four parallels to allow for proper results valuation.

For ozonation experiments ozone generator by a Xylem Water Solutions GmbH Herford, type OCS Modular 8 HC was used. The operating pressure was 0.5 bar, the gas flow of 0.08 m^3 h^{-1} and the capacity of the system was 8 g h^{-1}. The nominal concentration of ozone in the gas phase was 100 g Nm^{-3}. Ozone was passed into a glass laboratory bubble column (250 mL).

To determine biogas production of sludge, standard biodegradability assessment test in anaerobic conditions was applied with some minor modifications (ISO 11734, 2004). The increase of headspace pressure (hPa) in test vessels resulting from the production of CH_4 and CO_2 (biogas) was measured by the OxiTop® system at 39±1 °C (WTW Germany, 2008).

3. Results

Typical anaerobic biodegradability curves, expressed as biogas gain (mL), is shown in Figure 1. Curve drops at 162 hrs (7 days) as NaOH was added into the test solution, to adsorb evolved CO_2. Remaining volume of biogas is mainly CH_4. For a better clarity, summary of these results achieved during experiments are presented in Figure 2.

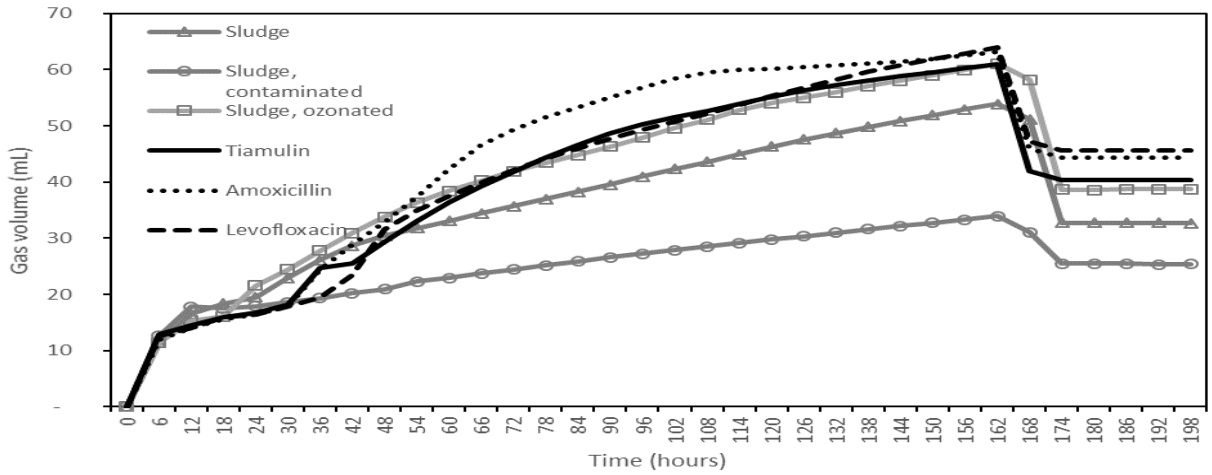

Figure 1. Biogas production for non-treated sludge, ozonated sludge, sludge contaminated with antibiotics (100 mg L^{-1}), and contaminated and subsequently ozonated sludge.

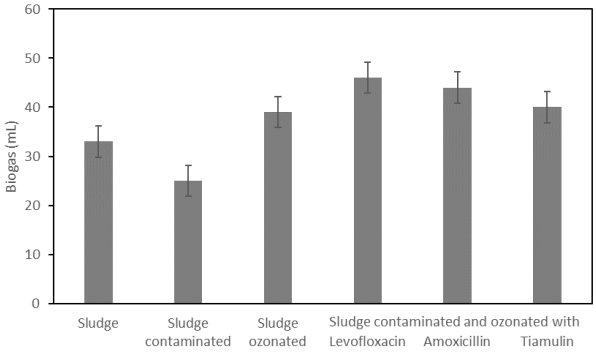

Figure 2. Summary results of biogas production for non-treated, contaminated, ozonated, contaminated and subsequently ozonated sludge.

Figure 2 shows, that biogas production is inhibited by the antibiotics, for about 24% for all antibiotics that we have used. Second column of Figure 2 shows an average biogas production when contaminated with antibiotics, all three falling in the range of ± 5%.

Ozonation of the waste sludge increases biogas production (18%). The ozone dose used (70 mg_{O3} g_{VSS}^{-1}) was quite low for a rather significant effect of biogas production enhancement. Past study (Ak et. al, 2013) demonstrated that anaerobic digestion of waste activated sludge, when supported with low ozone doses (1.33 mg_{O3} g_{VSS}^{-1}), improved the biogas production even by 100%.

On the other hand, ozonation also removes all inhibition effects and even enhances biogas production beyond the baseline biogas production of the non-contaminated sludge. There was 18% increase for levofloxacin and 13% for amoxicillin.

4. Conclusion

Results indicated that ozonation is a promising technology, not only to enhance biogas production of waste biological sludge but also to remove or at least suppress inhibitory effects of antibiotics that might be present in the sludge. When using ozonation, event at low doses (70 mg_{O3} g_{VSS}^{-1}), biogas production is enhanced for 25%. Inhibition of biogas production by antibiotics at doses of 100 mg L^{-1}, may be completely removed and biogas enhanced as there was no contamination present at all.

References

International organization for standardization (1995), International standard, ISO 11734:1995. Water quality - Evaluation of the "ultimate" anaerobic biodegradability of organic compounds in digested sludge - Method by measurement of the biogas production, International organization for standardization, Geneva.

Ak M.S., Muz M., Komesli O.T., Gökçay C.F. (2013), Enhancement of bio-gas production and xenobiotics degradation during anaerobic sludge digestion by ozone treated feed sludge, *Chemical Engineering Journal* **230**:499-505.

Wacławek, S.; Grübel, K.; Silvestri, D.; Padil, V.V.T.; Wacławek, M.; Černík, M.; Varma, R.S. (2019), Disintegration of Wastewater Activated Sludge (WAS) for Improved Biogas Production. *Energies* ***12***, 21.

Venturin B., Bonatto C., Damaceno F.M., Mulinari J., Fongaro G., Treichel H. (2019) Physical, Chemical, and Biological Substrate Pretreatments to Enhance Biogas Yield. In: Treichel H., Fongaro G. (eds) Improving Biogas Production. Biofuel and Biorefinery Technologies, vol 9. Springer, Cham

Almomani,F. Shawaqfah M., Bhosale R.R., Kumar A., Khraisheh M.A.M. (2017) Intermediate ozonation to enhance biogas production in batch and continuous systems using animal dung and agricultural waste, *International Biodeterioration & Biodegradation*, **119**, 176-187